Mechanical Properties of Concrete incorporating natural Pozzolanic Material Subjected to Crude Oil

Shaho Mahmoud Hama[1]

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Abstract

The paper shows the final findings of the effect of metakaolin on the strengths properties of concrete exposed to crude oil. Sulfate resistance Portland cement of V type was used and specimens of concrete were adjusted and subjected to a solution of concentrated crude oil. However, the samples are cured in a control media at immersion ages of (28, 56 & 120 days) with ambient temperature, then samples have been kept in curing water for comparisons purpose as well. The results explain that the use of metakaolin reinforces compressive, flexural and splitting resistance of concrete which is exposed to crude oil. The compressive strength reduction increased from 8.0% at (28 days) to 37.7% at (120 days) curing for normal weight concrete (NW) whereas the concrete incorporating metakaolin (MC) has a reduction of 6.0% at (28 days) & 29.3% at (120 days).

Key Words: Strength, Ordinary Portland cement, Metakaoline, Crude Oil

الخواص الميكانيكية للخرسانة المكونة من مواد البوزلانية الطبيعية معرضة للنفط الخام

شاهو محمود حمه

الخلاصة

يتضمن هذا العملِ نتائِج التحري عن تأثيرِ ميتاكاؤلين على بعض خواص الخرسانةِ المعرّضَة إلى النَفط الخامّ. وقد تم استخدام الاسمنت البورتلندي المقاوم (نوع V). بعد معالجة النماذج الخرسانية في الماء العادي بدرجةِ الحرارة الاعتيادية لعمر 28 يوم عرضت إلى ِ النفط الخامّ المُرَكَّزِ حتى أعمارِ الفحص 28, 56 و120 يوم، اضافة الى النماذج المرجعية المعالجة في الاحواض الماء العادي لأغراض المقارنة. إنّ النَتائِج الفحوصات اشارت الى ان استعمال ميتاكاؤلين يحسن من مقاومة الخرسانةِ المعرّضة إلى النفط الخامّ. لوحظ تناقص بمقاومة الانضغاط من 8.0% عند (28 يوم) الى 37.7% عند (120 يوم) بعد المعالجة للخرسانة الاعتيادية (NW)، بينما في الخرسانة الحاوية على ميتاكاؤلين (MC) تناقصت مقاومة الانضغاط 6.0% عند (28 يوم) الى 29.3% عند (120 يوم) بعد المعالجة .

1. Introduction

Crude oil is simply a raw oil which is found in depth of the earth beneath its surface. Its color varies from clear to black. Steel tanks and pipes have traditionally been used for storage and transportation of crude oil products around the world. But as a result of the critical shortage of steel plate and problems of serviceability and safety, large concrete structures, reinforced or pre-stressed, were built for the production, storage and transportation of oil. For warehousing reason, the changing steel into concrete is because the cost low of construction, maintenance. Concrete oil-storage tanks have many advantages if adequate impermeability could be assured without the use of expensive impermeable liners. Before 1914, many concrete tanks were built in the USA for storage of heavy oils and during the Second World War, the USA navy built concrete tanks for fuel oil Storage (Spamer , 1944; Shepard 1944). Though concrete storage tanks have been used for more than 80 years, even then, there is a lack of knowledge regarding the impact of petroleum products on concrete. To store petroleum products concrete tanks are used and this is a century old technique.

[1] *Assistant lecturer at the Department of Civil Engineering, University of Anbar.*

The usage of concrete in this context has led to many economic benefits and has paved way to enhance further study into the use of concrete on a comparatively larger scale (Shepard 1944). The main problems that restrict the successful use of concrete to store fuel oil are: the leakage of oils especially the lighter products (that having specific gravity 0.875 at a temperature (15˚C) through the pore structure, shrinkage cracks and joints (Lea, 2004; Matti, 1976).

Moreover, of course different types of crude oil have different amounts of sulphur content that in normal cases is in a formed compound (Ejeh, and Uche, 2009). Kline showed that aggressive medium for cement-based materials is the sulphurous compounds. Normally, the concrete mass that has exposure to sulphurous products is subjected to chemical reactions that expand the mortar fraction (Kline, 2004). The ettringite formation is the most expansion root cause & concrete/ mortar disruption raised by solutions of sulphate. Such kind of concerns could be only exacerbated by temperature changes. Studies by some researches showed that significantly agents affecting concrete characteristics contain curing conditions prior to moisture condition, and concrete exposure at the exposure time, cement type and crude oil storage temperature (Matti, 1976; Khaloo, *et al.,* 2005 and Richmond, et al., 1980).

Ejeh and Uche studied the effect of the crude oil spill on compressive strength of concrete materials. They both mentioned that the crude oil spillage effect on concrete strength properties is created with (OPC) that is used in concrete constructions in Nigeria and the results show (OPC) concrete is oversensitive to crude oil concentrations different solutions aggressiveness that led them to strength development low rates. Also, it is represented, the entire media whereas the control medium is including that led to increasing in concrete specimen's strength after (60 days) of immersion, however, the compressive strength development rate is low in the crude oil/water mix & crude oil (Ejeh, and Uche, 2009).

Based on short and long-term loading, the effect of crude oil on the compressive, flexural tensile and flexural tensile strength of concrete is investigated (Ramzi, 2000). They discovered that the crude oil absorption rate is high at an early stage of soaking, however, the rate decreases later. This confirms the reduction in the absorption by 30 to 40 % strength in specimens under loading versus unloaded specimens criteria". Onabolu worked on crude oil in which properties of concrete soaked and exposed at ambient temperature showing different values in concrete materials mechanical properties along with time (Onabolu, 1989). Additionally, he repeated that the variations in typical offshore concrete structure absorption characteristics & length change compressive strength which exposed to crude oil for one year usually came to terms the resistance and the storage tank structures serviceability. In the same year, he studied some properties of crude oil soaked concrete-II exposure at elevated temperatures of 45, 60 and 800 C, superimposed on the conditions of curing, has been studied and was found to affect the measured properties significantly. The results have shown that the mechanical properties of concrete exposed to hot crude oil were affected by such conditions as a mode of curing, moisture condition at the time of exposure, and exposure temperature (Onabolu, 1989).

2. Review of Pozzolanic Material Effect Review of Concrete Exposed to Crude Oil Properties

In vehicle service stations petroleum, products regularly come in contact with the surface flooring, water gets contaminated with petroleum products, that filtrate through the ground and then contaminates underground water. Because of the spillage of petroleum products the surface could rift, it creates water pollution, that it could affect marine animals. These are all few adverse effects which may lead to concrete deterioration. Fly-ash and silica fume are cheap and available hazardous waste. Silica industries improve the workability of concrete which also reduces the hydration reaction at early stages. Once these pozzolans are added, then they enable the concrete to react with $Ca(OH)_2$ to form additional calcium silicate hydrate which grows the density, and properly fill the pores, refine the pore structure and the permeability which leads to the better resistance (Folagbade *et al*., 2012). Actually, Fly ash and silica fume show comparatively poor characteristics at premature ages, but its pozzolanic reaction enhances the curing age and it also provides good resistance in aggressive media in concrete (Naik, 1998; Lam, 1989).

3. Objectives

The paper aims to concentrate and investigate the effect of metakaolin (natural pozzolanic material) on characteristic behavior of concrete exposed to crude oil.

4. Materials used

- **Cement:** Sulfate resistance Portland cement (Type V) is used. Total percentages for their oxides, the compound composition is according to the Iraqi specification requirement No.5/1984 as shown in Table 1.

Table 1. Chemical oxide composition and components of OPC

Chemical analysis	Test results %(By weight)	Iraqi specification Limits No.5/1984
MgO	1.93	5.0% (max.)
SO_3	2.19	2.5%(max.)
Fe_2O_3	3.18	–
CaO	62.07	–
SiO_2	21.60	
Al_2O_3	5.30	–
Ignition Loss (I.L)	1.78	4.0%(max.)
Main compounds (Bogue's equation)		
C_3S	47.16	–
C_2S	26.62	–
C_3A	6.43	–
C_4AF	9.97	–

- #Tests were carried out by state company of geological survy & mining.

Aggregate; the fine aggregate used is local sand, it meets Iraqi specification requirements No.45/1984 with respect to physical properties and the sieve analysis as shown in Table 2 and 3. Crushed coarse aggregate from a region located in Anbar governorate is used for all concret mixes in this study. The aggregates are conforming to the requirements of the Iraqi Specification No. 45-99. Specific gravity is equal to 2.79 and sulfate content is equal to 0.071%. Results of sieve analysis of coarse aggregate are shown in Table 4.

Table 2. Sand Grading and Iraqi specification limits No.45/1984

Sieve size (millimeter)	Passing %	Iraqi specification Limits: 45/1984 Passing % [Zone 1]
9.50	100	100
4.75	90	90– 00
2.36	75	60– 95
1.18	56	30–70
0.60	30	15–34
0.30	13	5–20
0.15	6	0–10

Table 3. Sand physical & chemical properties

Property	Results
Apperant specific gravity	2.5
Absorption%	2.2
Dry loose unit weight (kg/m^3)	1600
Sulphate content(SO_3)%	0.25
Material finer than 0.075 millimeter sieve %	2.3

- The test was implemented in Civil Engineering laboratory, University of Anbar.

Table 4. Coarse aggregate grading

Sieve size (millimeter)	Coarse aggregate Passing %	Iraqi Specification Limits: 45/1984
12.5	100	100
9.5	96	85-100
4.75	28	10-30
2.36	6	0-10
1.18	1.5	0-5

- **Metakaolin:** the metakaolin which used in this study, is obtained by calcination of kaolinitic clay at temperatures from 700 °C for one hour. The metakaolin used in this study is complying the activity of strength index with Portland cement requirements that are ASTM C311–05 & ASTM C618–05. The chemical analysis is presented in Table 5.

Table 5. Metakaoline Chemical Analysis

Oxides	% By weight	ASTM C618–03
SiO_2	52.38	Silicon dioxide (SiO_2) plus aluminum
Al_2O_3	37.31	oxide (Al_2O_3) plus iron oxide
Fe_2O_3	1.21	(Fe_2O_3)=70% (Min.)
CaO	1.68	–
MgO	0.3	–
K_2O	0.44	–

#Tests are carried out by state company of geological survy & mining.

- **Superplasticizer:** the superplasticizer, Ecuobet, is used in this paper which complies with ASTM 494-05. Type A and F are used in this study, in which its properties are shown in Table 6.
- **Mixing and Curing Water:** normal tap water is used for mixing and curing of specimens.
- **Crude oil:** Crude Oil is gained from North refinery & their viscosity is 6.3 at 25 ^{o} C.

Table 6. Properties of superplasticizer

Oxides	% By weight
Main action	Concrete super- plasticizer
Appearance	Liquid
Color	Brown
Specific gravity	1.1
Chloride content	Nil
Compatibility with cement	All type of Portland cement

5. Mixing of Concrete

The absolute design volume method is used to produce concrete of nominal mix of 1:1.5:3 and the water/cement ratio is 0.24. The dosage of SP is fixed 2.5% (% weight of cement) and kept constant for all the mixes. The percentage of metakaolin is 7.5% from weight of cement, as shown in Table 7 Mixing operations are made in the concrete laboratory in the civil engineering department, University of Anbar. A 0.1m^3 pan mixer is used for mixing purpose. The coarse aggregates and cement are being mixed them dry until a homogenous dry mix is obtained. The water is added, then the mixing continued until final mix is obtained. The concrete mix is poured in three layers in the molds. Finally, an electrical vibrator made compaction for not more than 10 sec.

Table 7. Mix Proportion

Material	Content kg/m^3
Cement	400
Sand	600
Gravel	1200
Water	96
S.P	10
Metakaolin	30

6. Preparation of Specimens and Curing

The cubic molds of size of 100×100×100 mm and 100×100×500 prism molds lightly oiled are filled with fresh concrete and compacted by using vibrating table. For each concrete mix, forty eight specimens are cast, three cubic specimens for density test, three for compressive strength test, three cylinder for splitting tensile strength and three prism for modulus of rupture test. After each casting the molds is normally covered by polyethylene sheet and then it is kept in the laboratory environment for one day and after that the specimens are be molded together and put in the water tanks for no less than 28 days. Then, the reference specimens remain in the water and others remove to crude oil tanks until required age of test (28, 56 and 120 days) (see Figure 1).

Figure 1. Specimens of concrete were subjected to a solution of concentrated crude oil.

7. Hardened Concrete Tests

- **Compressive Strength:** concrete compressive strength was measured by using (100 ×100× 100mm) cubes for 28–day age according to B.S.1881. The three specimens for each mix is regarded as adopted one.
- **Flexural Tensile Strength**: the modulus of rupture test was carried out using (100 ×100× 500 mm) prisms, loaded at 450 mm span with one points loading under a hydraulic machine. The test is carried out according to ASTM C293–05, using three concrete prisms and the average of three results is adopted. (see Figure 2)

Figure 2. The modulus of rupture test

- **Splitting Tensile Strength**: this test was performd according to ASTM C496-03, using 150*300 mm concrete cylinders.
- **Unit Weight (Density):** Average of three (100x100x100mm) cubes was used to determine hardened unit weight.

8. Test Results and Discussion

- **Compressive Strength**

Figure 3 shows the variation of compressive strength with time. As it is evident from Table 8. the curing media has an effect on the concrete cubes compressive strength. The water values remained compressive strength in a systematic increase as the curing ages increased for both concrete types. It is not astonishing when cement strength based materials cured in water is increasing with age. The variation in results under the two curing conditions might be assigned to reaction of chemical effect which happening in solution of the crude oil, however, it is no present in water. The strength reductions can be related to the pattern of crude absorption. The crude oil absorption into the microstructure of the matrix of concrete may have caused dilation of the gel and weakening of the cohesive forces in the paste and hence low strength development of the concrete cured media. (Onabolu, 1989; Pihlajavaara, 1974). Additionally, Onabolu showed the decrease in energy of surface that is reasoned by crude oil adsorption onto C-S-H gel surface might also have contribution to the material compressive strength reduction. In comparison with compressive strength of specimens kept in control media, the compresive strength reduction increased from 8.0% at (28 days) to 37.7% at (120 days) curing for normal weight concrete (NW) whereas the concrete incorporating metakaoline (MC) has reduction of 6.0% at (28 days) & 29.3% at (120 days). Accordingly, it could be mentioned that crude oil medium that is undiluted has in general, bad effect upon concrete at all curing ages i.e., short, medium and longer periods. The variations trend in media aggressiveness might be connected to conductivity & concentration of sulfur that other chemical reactions & earlier identified ions might lead to paste composition alteration with mono-sulfate phase rendering to ettringite as well as bond loss between the paste of cement and thereby of aggregates creating overall loss in the strength of concrete. It can be noticed that the metakaoline usage improves with curing age & also in aggressive media in concrete, it provides good resistance. This results agreed with another researcher who used another type of pozzalanic material (Jasim and Jawad, 2010)

Table 8. Compresive strength result of the test specimens

Liquid	Age (days)	Compressive strength (MPa)	
		NW	MC
Water	28	41.9	63.1
	56	44.9	66.7
	120	47.0	70.6
Crude oil	28	38.5	59.3
	56	35.1	53.0
	120	29.3	49.9

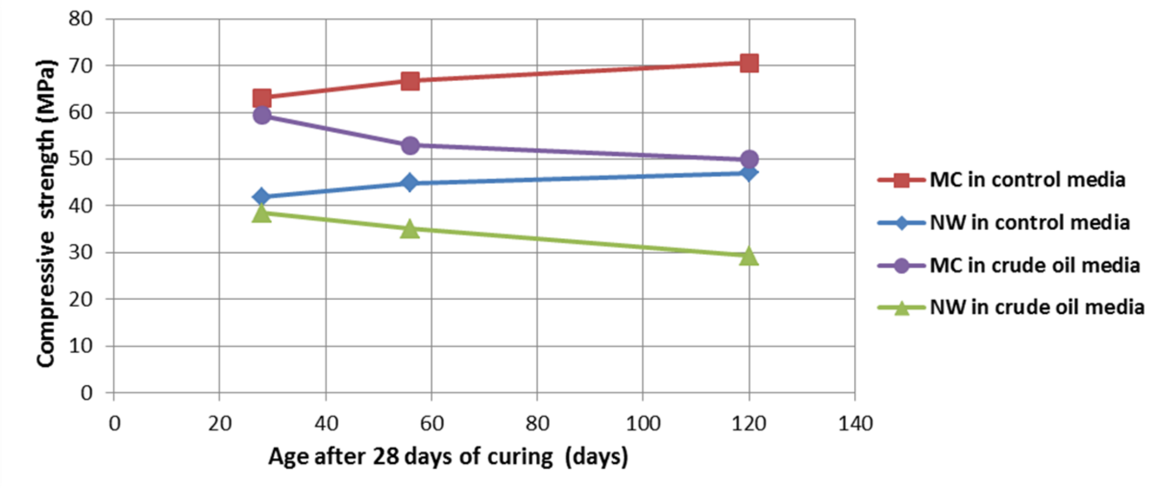

Figure 3. Result of compressive strength

- **Flexural and splitting Tensile Strengths**

The flexural and splitting strengths of NW and MC test results of exposed to crude oil are given in Table 9. While Figures 4 and 5 show the change in flexural and splitting tensile strengths, respectively, of specimens exposed to crude oil and those cured in water at the same age. In comparison to the flexural strength of specimens kept in control media, the reduction in flexural strength increased from 2.1% at (28 days) to 6.1 % at (120 days) of curing for NW when MC reduction has 1.9 % at (28 days) & 7.4% at (120 days). While the loss in splitting strength of specimens was 1.3% at (28 days) to 10.4 % at 120 days for NW whereas for MC was of 0.3 % at 28 days and 0.8% at (120 days). The splitting strength of MC seems the least affected by crude oil media.

Table 9. Flexural and Splitting Tensile Strengths results of the test specimens

Liquid	Age (days)	Flexural Tensile Strength (MPa)		Splitting Tensile Strength (MPa)	
		NW	MC	NW	MC
Water	28	4.20	5.23	2.36	3.11
	56	4.46	5. 37	2.76	3.38
	120	4.60	5.40	2.97	3.63
Crude oil	28	4.11	5.13	2.33	3.10
	56	4.26	5.09	2.67	3.30
	120	4.32	5.00	2.66	3.60

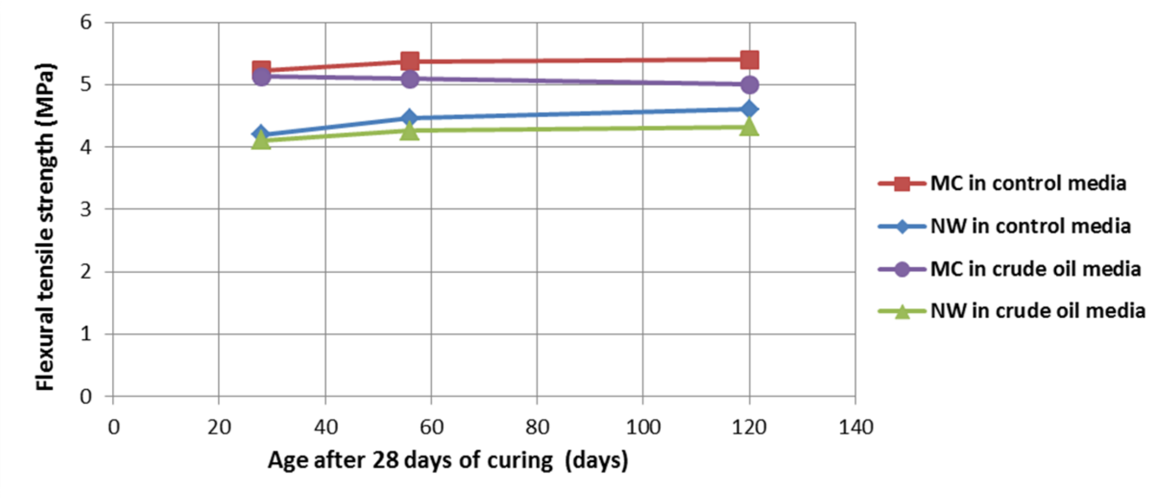

Figure 4. Flexural tensile strength variations with time

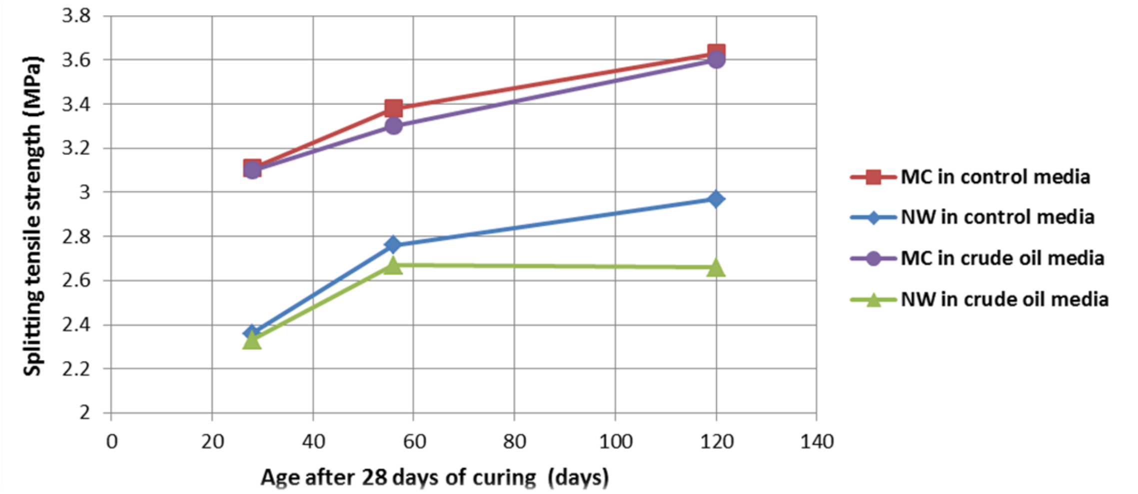

Figure 5. Splitting tensile strength variations with time

- **Unit Weight (Density)**

Test results of density of NW and MC exposd to crude oils are given in Table 10. Figure 6 shows the change in dry unit weight of the specimens exposed to crude oil compared with those cured in water at the same age. Based on the experimental results, it can be noticed the reduction in unit weight of specimens which is kept in control increased from 0.54% at 28 days to 1.36 % at 120 days of curing for NW whereas for MC reduction has 0.49 % at (28 days) & 1.27% at (120 days).

Table 10. Dry unit weight results of the test specimens

Liquid	Age (days)	Dry unit weight (kg/m^3)	
		NW	MC
Water	28	2416	2470
	56	2428	2498
	120	2433	2510
Crude oil	28	2403	2458
	56	2410	2482
	120	2400	2478

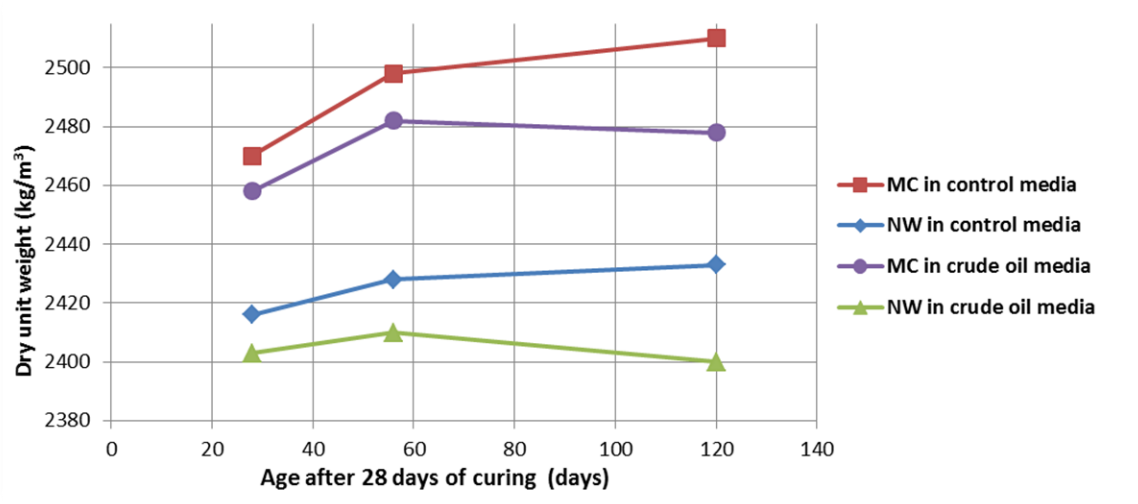

Figure 6. Dry unit weight variations with time

9. Conclusions

In regards to the test result of the paper, below points are concluded:

1. All specimens of concrete cured in a medium such as water that is steadily increased in a strength compressive as ages increase from (28, 56) & (120 days). The compresive strength reduction increased from 8.0% at (28 days) to 37.7% at (120 days) curing for normal weight concrete (NW) whereas the concrete incorporating metakaoline (MC) has reduction of 6.0% at (28 days) & 29.3% at (120 days).
2. Concrete has less opposition to environmental & chemical aggressions as they showed slow development of compressive strength in all exposure ages once it is compared to a medium such as water, i.e., a control medium.
3. The results of test for compressive strength follows similar pattern of flexural and splitting strengths, but with a percent of reduction in compressive strength was more than the reduction in tensile strengths.
4. Metakaoline usage has improved the strengths of concrete specimens exposed to crude oil.

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